This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images, please do not report the images to the Image Problem Mailbox.

MODIFIED θ-ALUMINA-SUPPORTED NICKEL REFORMING CATALYST AND ITS USE FOR PRODUCING SYNTHESIS GAS FROM NATURAL GAS

FIELD OF THE INVENTION

The present invention relates to a modified Θ-Al_2O_3-supported nickel reforming catalyst and its use for producing synthesis gas from natural gas. More particularly, the present invention is to provide a nickel reforming catalyst expressed by the following formula 1, having improved coke resistance, high-temperature catalysis stability and catalytic activity, which is prepared by coating nickel or mixture of nickel and cocatalyst (M_1-M_2-Ni) on a Θ-Al_2O_3 support modified with metal (M_3-M_4-ZrO_2/Θ-Al_2O_3), and its use for producing synthesis gas from natural gas through steam reforming, oxygen reforming or steam-oxygen reforming,

$$M_1\text{-}M_2\text{-}Ni/M_3\text{-}M_4\text{-}ZrO_2/\Theta\text{-}Al_2O_3 \qquad (1)$$

wherein M_1 is an alkali metal; each of M_2 and M_3 is an alkaline earth metal; and M_4 is a IIIB element or a lanthanide.

BACKGROUND OF THE INVENTION

Steam reforming, which produces a mixture (synthesis gas) of hydrogen and carbon monoxide from methane (natural gas), has become an important and fundamental chemical industrial process from long time ago. Synthesis gas produced by steam reforming of methane is widely used for producing methanol, hydrogen,

ammonia, etc. Recently, it has been used for producing liquid fuel or oxygen-including compounds.

The biggest problem in the steam reforming is deactivation of reforming catalyst due to deposition of carbon. The carbon deposition can be calculated thermodynamically from molar ratios of hydrogen to carbon and oxygen to carbon in the product. Therefore, in steam reforming of methane, excess amount of steam is required to increase molar ratios of hydrogen to carbon and oxygen to carbon, in order to prevent deactivation of reforming catalyst. This promotes an aqueous gasification enough to obtain a synthesis gas with molar ratio of hydrogen to carbon monoxide larger than 3:1. Therefore, this process may be suitable for producing ammonia or high-concentration hydrogen. The current industrial steam reforming process of methane is being carried out under the condition of 730-860℃ of a temperature, 20-40 atm of a pressure and 1:4-6 of methane-to-steam molar ratio.

And, for the industrial catalyst for the steam reforming, nickel catalyst is used dominantly. A superior industrial reforming catalyst should have coke resistance and thermal and mechanical stability. For this purpose, selection of suitable support such as α-alumina is very important.

The inventors suggested reforming reactions using modified zirconia-supported nickel catalyst.[Korea Patent Application No. 99-50013; Korea Patent Application No. 2000-0054443; & Korea Patent Application No. 2000-0057688]. Korea Patent Application No. 99-50013 discloses a modified zirconia-supported nickel catalyst and carbon dioxide reforming using it. Korea Patent Application No. 2000-0054443 discloses a cerium-modified zirconia-supported nickel catalyst and steam reforming using it. Further, Korea Patent Application No. 2000-0057688 discloses a modified

zirconia-supported nickel catalyst and steam-oxygen reforming using it. The modified zirconia-supported nickel catalyst showed better activity and stability than those of conventional reforming catalysts when used in carbon dioxide reforming, steam reforming and steam-oxygen reforming even under severe condition (high space velocity and low steam-to-methane ratio) and at high temperature. Despite of good activity and stability, zirconia is not suitable to be used in reforming catalyst, because it is more expensive than alumina. Accordingly, it is required to use the more cost-effective Θ-Al_2O_3 support and modify it with zirconia. Then, if it is coated with nickel catalyst, an inexpensive catalyst with good activity and stability can be obtained.

SUMMARY OF THE INVENTION

Inventors have developed a nickel reforming catalyst by coating Θ-Al_2O_3 base support with zirconia modified with alkaline earth metal (M_3) and IIIB element or lanthanide metal (M_4), and coating nickel and alkali metal (M_1) or alkaline earth metal (M_2) cocatalyst. When this reforming catalyst was used in various reforming reactions of natural gas, i.e., steam reforming, oxygen reforming or steam-oxygen reforming, it has showed equal or superior activity and stability compared with the modified zirconia-supported nickel catalyst we had suggested in Korea Patent Application No. 99-50013.

Accordingly, an object of the present invention is to provide a nickel reforming catalyst using Θ-Al_2O_3 as base support, and its use for producing synthesis gas through reforming reaction.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is to provide a nickel reforming catalyst expressed by the following formula 1, which is used for producing synthesis gas mixture of carbon monoxide and hydrogen from natural gas,

$$M_1\text{-}M_2\text{-}Ni/M_3\text{-}M_4\text{-}ZrO_2/\Theta\text{-}Al_2O_3 \qquad (1)$$

wherein M_1 is an alkali metal; each of M_2 and M_3 is an alkaline earth metal; and M_4 is a IIIB element or a lanthanide.

Synthesis gas mixture of carbon monoxide and hydrogen may be produced from methane in the presence of the nickel reforming catalyst by steam reforming, oxygen reforming or steam-oxygen reforming, under the condition of 0-6 of methane-to-steam molar ratio, 0-1 of methane-to-oxygen molar ratio, 600-1000℃ of a reaction temperature, 0.5-20 atm of a reaction pressure and 1,000-1,000,000cc/hr·g-cat of a space velocity.

Hereunder is given a more detailed description of the present invention. This invention relates to a reforming catalyst expressed by formula 1 and its use for producing synthesis gas by steam reforming, oxygen reforming or steam-oxygen reforming of natural gas.

The modified Θ-Al_2O_3-supported nickel reforming catalyst according to the present invention is prepared by coating a modified zirconia (M_3-M_4-ZrO_2) on Θ-Al_2O_3 base support and coating nickel and cocatalyst (M_1-M_2-Ni) on it. Here, nickel is added preferably in the range of 3 to 20 wt.% based to Θ-Al_2O_3. Each of M_1 and M_2 cocatalysts is added preferably in the range of 0 to 0.2 and 0 to 4 molar ratios based to

nickel, respectively. Each of M_3 and M_4 is added preferably in the range of 0 to 1.0 and 0.01 to 1.0 molar ratios based to zirconium (Zr), respectively. Zirconia (ZrO_2) is added preferably in the range of 0.01 to 1.0 molar ratio based to Θ-Al_2O_3.

M_1 is an alkali metal chosen from sodium, potassium and cesium; each of M_2 and M_3 is an alkaline earth metal chosen from calcium, magnesium and strontium; and M_4 is a IIIB element chosen from yttrium, lanthanum and cerium, or lanthanide, wherein M_3 and M_4 are cocatalysts for enhancing coke resistance and catalytic activity.

The reforming catalyst according to the present invention may be prepared by coprecipitation, precipitation, sol-gel method, molten-salt or impregnation method. When Θ-Al_2O_3 is modified with zirconia to obtain support, coprecipitation or sol-gel method is preferable. When nickel and cocatalyst are coated on the support, molten-salt and impregnation methods are preferable.

Preparation of modified Θ-Al_2O_3 support through coprecipitation is as follows. 1M zirconyl chloride aqueous solution is purified by recrystallization from hydrochloric acid. 1M nitrate solution of the metal to be modified on the Θ-Al_2O_3 base support is added to this solution. After strongly stirring the mixture at 50-70℃ for 4-8hr, 29.8% ammonia water is added until pH reaches 10. The precipitate is filtered and washed with 5% ammonia water until no chloride ion is observed. It is further washed with distilled water. The filtered precipitate is placed in a drying oven and dried at 90-100℃ for 10-12hr. Then, it is put in a furnace and calcined in 700-900℃ of air for 7-9 hr to obtain the modified Θ-Al_2O_3 support.

Preparation of nickel- and cocatalyst-supported modified Θ-Al_2O_3 support through impregnation is as follows. Modified Θ-Al_2O_3 support powder is added in distilled water and stirred to obtain a slurry. 1M nitrate solution of nickel and the metal

used as cocatalyst is added to this slurry. The mixture is stirred at 25℃ for 5-7hr. Then, the flask containing this mixture solution is connected to a rotary vacuum evaporator in order to evaporate water under pressure of 90-120 Torr and temperature of 70-90℃. The obtained catalyst precursor powder is dried in a drying oven at 100℃ for 12hr. and calcined at 400-500℃ in air for about 4hr to obtain the nickel reforming catalyst.

Preparation of nickel- and cocatalyst-supported modified Θ-Al_2O_3 support through molten-salt method is as follows. The fact that nickel and cocatalyst metal precursor have low melting temperature is used. In order to obtain uniform and thin coating of metal component on the modified Θ-Al_2O_3 support, the support powder and the metal precursor powder is finely ground and mixed well at room temperature. Then, the metal precursor component is decomposed through a well-defined heat treatment process to obtain the catalyst. The heat treatment process is as follows. All nitrates in the catalyst precursor powder are melt by heating it at 2℃/min from room temperature to 400℃ under argon flow of 100mL/min in a furnace. The nitrates are decomposed at 400℃ for 4hr. Then, after changing argon flow to dry air flow, the temperature is increased to 650℃ at 5℃/min. The product is treated for 4hr at 650℃. The typical catalyst obtained from this method is Ni-Ca/Ce-ZrO_2/Θ-Al_2O_3 catalyst, which is prepared by using nitrates of nickel (melting point: 56.7 ℃) and calcium (melting point: 39.7 ℃) as metal precursor.

The above methods are only examples of preparing modified Θ-Al_2O_3-supported nickel reforming catalysts according to the present invention. Other known preparing methods may be used if necessary.

Reaction condition of producing synthesis gas from natural gas using the nickel

reforming catalyst according to the present invention is as follows.

The nickel reforming catalyst expressed by formula 1 can be used in steam reforming, oxygen reforming or steam-oxygen reforming to prepare synthesis gas mixture of carbon monoxide and hydrogen from methane. In the reforming reactions, methane-to-steam molar ratio is preferred to be 0-6, and methane-to oxygen molar ratio is preferred to be 0-1. To be more specific, in the steam reforming, the methane-to-steam molar ratio is preferred to be 1-6; in the oxygen reforming, the methane-to-oxygen molar ratio is preferred to be 0.1-1; and in the steam-oxygen reforming, the methane-to-steam molar ratio is preferred to be 1-5 and the methane-to-oxygen molar ratio is preferred to be 0.1-1. The reaction temperature is 600-1000℃ and the reaction pressure is 0.5-20 atm. The reaction gas is injected at 1,000-1,000,000cc/hr·g-cat of space velocity.

As described above, the present invention provides a new industrial catalyst, which has equal or superior activity and stability compared to the expensive conventional modified zirconia-supported nickel reforming catalyst, by coating modified zirconia on Θ-Al_2O_3 support and supporting nickel or mixture of nickel and cocatalyst on the support.

The following examples are intended to be illustrative of the present invention. However, they should not be construed as limiting the scope of this invention.

Preparing Example 1: Preparation of Θ-Al_2O_3 support modified with alkaline earth metal and zirconia

Modified Θ-Al_2O_3 support was prepared by coprecipitation using alkaline earth metal, such as calcium and magnesium, and zirconia.

Firstly, zirconyl chloride (Aldrich, 98%) was diluted to 1M aqueous solution and purified by recrystallization from hydrochloric acid. After mixing the result with 1M alkaline earth metal nitrate solution, the mixture was strongly stirred at 60℃ for 6hr. After adding Θ-Al_2O_3 support and 29.8% ammonia water (Fisher Scientific) until pH reaches 10, the precipitate was filtered and washed with 5% ammonia water until no chloride ion was detected. Then, it was washed with distilled water. The filtered precipitate was dried at 100℃ for 12hr in a drying oven. The obtained powder was finely ground in mortar, and calcined in 900℃ of air for in a furnace to obtain modified Θ-Al_2O_3 supports. The obtained modified Θ-Al_2O_3 supports were Ca-ZrO_2/Θ-Al_2O_3 (Ca/Zr=1/2) and Mg-ZrO_2/Θ-Al_2O_3 (Mg/Zr=1/4). The content of Ca-ZrO_2 and Mg-ZrO_2 was 5 wt.% relative to Θ-Al_2O_3.

Preparing Example 2: Preparation of Θ-Al_2O_3 support modified with ⅢB element or lanthanide and zirconia

Modified Θ-Al_2O_3 support was prepared by sol-gel method using ⅢB element or lanthanide, such as yttrium, lanthanum and cerium, and zirconia.

Nitrate of the metal component to be modified was added to 1L of distilled water at 20℃, so that its molar ratio against zirconia is 1:4. After dissolving uniformly for 5hr, Θ-Al_2O_3 support was added and molar equivalent of citric acid (against the metal nitrate) was added at the same temperature. After completely dissolving for 6hr, molar equivalent of ethylene glycol was added and the mixture was stirred for 6hr. Then, the mixture solution was condensed to highly viscous phase by suction-filtering at 80-100℃, and was dried in a microwave oven. The dry support powder was finely ground in mortar, and was calcined in 300℃ of air for 5hr, and then in 900℃ of air for

5hr in a furnace. The obtained modified Θ-Al_2O_3 supports were Ce-ZrO_2 (1:4)/Θ-Al_2O_3, La-ZrO_2 (1:4)/Θ-Al_2O_3 and Y-ZrO_2 (1:4)/Θ-Al_2O_3. The content of Θ-Al_2O_3 modifying component was set to be 5 wt.%.

Preparing Example 3: Preparation of Θ-Al_2O_3 support modified with alkaline earth metal, ⅢB element or lanthanide and zirconia

Θ-Al_2O_3 support modified with an alkaline earth metal, ⅢB element or lanthanide and zirconia was prepared by coprecipitation as in Preparing Example 2. The obtained modified Θ-Al_2O_3 support was Ce-Mg-ZrO_2/ Θ-Al_2O_3, and metal content was 20 mol% against zirconia. The content of Ce-Mg-ZrO_2 was set to be 5 wt.% against Θ-Al_2O_3.

Examples 1-10: Preparation of nickel reforming catalyst by impregnation

Nickel and cocatalyst were impregnated on the modified Θ-Al_2O_3 supports prepared in Examples 2 & 3.

Firstly, 20g of modified Θ-Al_2O_3 support powder was put in a 500mL round-bottom flask containing 200mL of distilled water. After making zirconia slurry by stirring this mixture, 1M nickel nitrate solution and cocatalyst component was added and stirred for 6hr at 25℃. Then, the flask containing the solution was connected to a rotary vacuum evaporator. The rotary vacuum evaporator was rotated under 100 Torr and 80℃ to evaporate water. The obtained catalyst precursor powder was dried in 100℃ of drying oven for 12hr. Then, it was calcined in 500℃ of air in a furnace for 4hr to obtain the modified Θ-Al_2O_3-supported nickel reforming catalyst.

In Ni/Ce-ZrO_2 (1:4)/Θ-Al_2O_3 obtained from the impregnation, Ce-ZrO_2 content

was 5 wt.% against Θ-Al_2O_3 support, and the nickel content was 3 wt.% (Example 1), 6 wt.% (Example 2), 12 wt.% (Example 3) and 15 wt.% (Example 4) against Θ-Al_2O_3. Other than Ni/Ce-ZrO_2 (1:4)/Θ-Al_2O_3, Ni/La-ZrO_2 (1:4)/Θ-Al_2O_3 (Example 5), Ni-Ca (1:1)/Ce-ZrO_2 (1:4)/Θ-Al_2O_3 (Example 6), Ni-Mg (1:1) /La-ZrO_2 (1:4)/Θ-Al_2O_3 (Example 7), Ni-Ca (1:1)/Y-ZrO_2 (1:4)/Θ-Al_2O_3 (Example 8), Ni-Ca (1:1)/Ce-Mg-ZrO_2 (1:1:3)/Θ-Al_2O_3 (Example 9) and Ni-Ca-Cs (1:1:0.1)/La-ZrO_2 (1:4)/Θ-Al_2O_3 (Example 10) were prepared. In these catalysts, the nickel content was set to be 12 wt.% against Θ-Al_2O_3.

Comparative Examples 1-4: Preparation of Ni/Ce-ZrO_2 (1:4)/Θ-Al_2O_3, Ni/Θ-Al_2O_3, Ni/α-Al_2O_3 and Ni/$MgAl_2O_4$ catalysts

As catalysts for comparing reforming activity and catalytic stability against those of the catalyst according to the present invention, Ni/Ce-ZrO_2 (1:4)/Θ-Al_2O_3 (Comparative Example 1), Ni/Θ-Al_2O_3 (Comparative Example 2), Ni/α-Al_2O_3 (Comparative Example 3) and Ni/$MgAl_2O_4$ (Comparative Example 4) were prepared.

Ni/Ce-ZrO_2 (1:4)/Θ-Al_2O_3 of Comparative Example 1 was prepared by the method of Example 2, and the nickel content was 2 wt.% against Θ-Al_2O_3. Ni/Θ-Al_2O_3 of Comparative Example 2 was prepared by precipitation, and the nickel content was 3 wt.% against Θ-Al_2O_3. Ni/α- Al_2O_3 of Comparative Example 3 and Ni/$MgAl_2O_4$ of Comparative Example 4 were prepared by impregnation, and the nickel content was 15 wt.% against Θ-Al_2O_3. α-Alumina was purchased from Strem Chemical (US) and magnesium aluminate was purchased from Alpha Chemical. In these catalysts, nickel was supported through impregnation and they were calcined in 500℃ of air for 4hr.

Experimental Example 1: Determination of reforming activity of nickel reforming catalyst in steam reforming of methane

Steam reforming of methane was performed in order to compare nickel reforming catalysts of Examples 1-10 with the catalysts of Comparative Examples 1-4. Catalytic activity was determined by the following method and the result is summerized in Table 1.

Typical fixed bed catalytic reaction equipment manufactured at laboratory was used in catalytic activity determination. Firstly, catalyst was made to pellet having 1-2mm particle size. After grinding the pellet in mortar, catalyst particles of 20-40 mesh was sieved and filled in a reactor. It was reduced with 5% hydrogen at 700℃ for 2hr. 1:1 Mixture of methane and steam was injected into the reactor. The temperature of the reactor was regulated by an electric heater and a programmable thermostat (Hanyoung Electronics, HY P-100) to 600-1,000℃. Unless stated otherwise, gas was injected at 72,000cc/hr·g-cat of space velocity when considering methane and steam only, using a mass flow controller. Composition of gas before and after synthesis gas production was analyzed with GC (Chrompack, CP 9001) directly connected to the reactor. A column (Chrompack, CarboPLOT P7) was used for gas separation. Activity of the reforming catalyst was measured with time at 750℃ and atmospheric pressure in order to determine its activity and thermal stability at high temperature. Initial activity and activity after 12hr were determined from hydrogen yield in the product and methane conversion. The hydrogen yield was obtained from ratio of theoretical hydrogen concentration when 1 mol of methane reacts with 1 mol of steam to produce 3 mol of hydrogen and the actual hydrogen concentration. The result is shown in Table 1.

The catalytic activity ratio was determined by Equation 1.

Equation 1

$$A = \frac{\textit{Methane conversion after 15hr at 750°C}}{\textit{Initial methane conversion at 750°C}}$$

$$B = \frac{\textit{Hydrogen yield after 15hr at 750°C}}{\textit{Initial hydrogen yield at 750°C}}$$

Table 1

Classification	Reforming Catalyst	Nickel Content* (wt.%)	750℃, Initial Activity		750℃, After 15hr		Catalyst Activity Ratio (A/B)
			X (CH_4)* *(%)	H_2 Yield (%)	X (CH_4)* *(%)	H_2 Yield (%)	
Ex. 1	Ni/Ce-ZrO_2/ Θ-Al_2O_3	3	71.2	71.3	70.9	71.0	1.00/1.00
Ex. 2	Ni/Ce-ZrO_2/ Θ-Al_2O_3	6	76.1	76.2	75.5	75.7	0.99/0.99
Ex. 3	Ni/Ce-ZrO_2/ Θ-Al_2O_3	12	82.3	82.3	82.5	82.4	1.00/1.00
Ex. 4	Ni/Ce-ZrO_2/ Θ-Al_2O_3	15	76.3	76.4	76.5	76.6	1.00/1.00
Ex. 5	Ni/La-ZrO_2/ Θ-Al_2O_3	12	72.7	73.0	71.5	72.6	0.98/0.99
Ex. 6	Ni-Ca/Ce-ZrO_2 /Θ-Al_2O_3	12	77.3	77.9	77.2	77.6	1.00/1.00
Ex. 7	Ni-Mg/La-ZrO $_2$/Θ-Al_2O_3	12	70.4	71.0	70.6	71.4	1.00/1.00
Ex. 8	Ni-Ca/Y-ZrO_2/ Θ-Al_2O_3	12	72.3	72.8	69.5	70.8	0.96/0.97
Ex. 9	Ni-Ca/Ce-Mg-ZrO_2/Θ-Al_2O_3	12	75.7	76.5	76.0	76.8	1.00/1.00

Classification	Reforming Catalyst	Nickel Content* (wt.%)	750℃, Initial Activity		750℃, After 15hr		Catalyst Activity Ratio (A/B)
			X (CH_4)* *(%)	H_2 Yield (%)	X (CH_4)* *(%)	H_2 Yield (%)	
Ex. 10	Ni-Ca-Cs/La-ZrO_2/Θ-Al_2O_3	12	68.8	70.2	66.1	67.8	0.96/0.97
Com. Ex. 1	Ni/Ce-ZrO_2/Θ-Al_2O_3	2	2.3	2.8	0.0	0.0	0.00/0.00
Com. Ex. 2	Ni/Θ-Al_2O_3	3	1.6	1.8	0.0	0.0	0.00/0.00
Com. Ex. 3	Ni/α-Al_2O_3	15	51.1	57.5	23.2	28.7	0.45/0.50
Com. Ex. 4	Ni/$MgAl_2O_4$	15	62.0	64.2	31.8	37.1	0.51/0.58

Note:

*Nickel Content (wt.%): against Θ-Al_2O_3

**X (CH_4): methane conversion

As shown in Table 1, Ni/Ce-ZrO_2/Θ-Al_2O_3 showed initial methane conversion as large as 71-82% when the nickel content was in the range of 3 wt.% (Example 1)-15 wt.% (Example 4). And, the methane conversion was maintained almost after 15hr. The initial hydrogen yield of larger than 71% was also maintained almost after 15hr. Because these activity and stability is for a severe condition where methane-to-steam ratio is 1, higher methane conversion is expected for actual steam reforming operation, where excess steam is used. Further, much better stability is expected in the presence of excess steam. All of Ni/La-ZrO_2/Θ-Al_2O_3 (Example 5), Ni-Ca/Ce-ZrO_2/Θ-Al_2O_3 (Example 6), Ni-Mg/La-ZrO_2/Θ-Al_2O_3 (Example 7), Ni-Ca/Y-ZrO_2/Θ-Al_2O_3 (Example 8), Ni-Ca/Ce-Mg-ZrO_2/Θ-Al_2O_3 (Example 9) and Ni-Ca-Cs/La-ZrO_2/Θ-Al_2O_3 (Example 10) showed initial methane conversion larger than 69% and initial hydrogen

yield larger than 70%. Also, they showed good stability with time. Therefore, they make good steam reforming catalysts.

On the contrary, Ni/Ce-ZrO2/Θ-Al_2O_3 (Comparative Example 1) with 2 wt.% of nickel showed initial methane conversion and hydrogen yield lower than 3%, and showed no activity after 15hr. It is shown that high activity is obtained only when the nickel content is larger than 3 wt.% for steam reforming. Also, Ni/Θ-Al_2O_3 (Comparative Example 2) with 3 wt.% of nickel showed initial methane conversion and hydrogen yield lower than 2%. Therefore only modified Θ-Al_2O_3 shows good activity. Ni/α-Al_2O_3 of Comparative Example 3 and Ni/$MgAl_2O_4$ of Comparative Example 4 showed initial methane conversion lower than 62% and the activity decreased below 50% after 15hr. Considering that Ni/$MgAl_2O_4$ is a widely used catalyst, the catalyst according to the present invention, which shows much superior activity and stability, will be able to replace it. The catalyst according to the present invention is also advantageous in terms of cost, because only 5 wt.% of modifying component is applied on Θ-Al_2O_3base support.

Experimental Example 2: Determination of reforming activity of nickel catalyst in oxygen reforming of methane

Oxygen reforming activity of nickel reforming catalysts prepared in Examples 1-10 and catalysts prepared in Comparative Example 1-4 was determined as follows.

The catalytic activity was determined as in Testing Example 1. However, oxygen was used instead of steam. Methane-to-oxygen molar ratio was set to 0.5. Gas was injected at 54,000cc/hr·g-cat of space velocity using a mass flow controller (MKS Instrument).

Activity and thermal stability of the reforming catalyst at high temperature were determined at 750℃ and atmospheric pressure. Initial activity and activity after 200min were determined by hydrogen yield in the product and methane conversion. The catalyst activity ratio was determined by Equation 2. The methane conversion and hydrogen yield are summerized in Table 2. The hydrogen yield in Table 2 is expressed in percentage of hydrogen partial pressure against 2 equivalents of methane partial pressure before reaction.

Equation 2

$$A = \frac{\textit{Methane conversion after } 200\,\text{min } \textit{at } 750°C}{\textit{Initial methane conversion at } 750°C}$$

$$B = \frac{\textit{Hydrogen yield after } 200\,\text{min } \textit{at } 750°C}{\textit{Initial hydrogen yield at } 750°C}$$

Table 2

Classification	Reforming Catalyst	Nickel Content* (wt.%)	750℃, Initial Activity		750℃, After 200min		Catalyst Activity Ratio (A/B)
			X (CH_4)** (%)	H_2 Yield (%)	X (CH_4)** (%)	H_2 Yield (%)	
Ex. 1	Ni/Ce-ZrO_2/Θ-Al_2O_3	3	89.4	84.3	89.4	85.1	1.00/1.01
Ex. 2	Ni/Ce-ZrO_2/Θ-Al_2O_3	6	89.1	84.2	89.2	85.0	1.00/1.01
Ex. 3	Ni/Ce-ZrO_2/Θ-Al_2O_3	12	89.7	84.3	89.7	84.4	1.00/1.00

Classification	Reforming Catalyst	Nickel Content* (wt.%)	750℃, Initial Activity		750℃, After 200min		Catalyst Activity Ratio (A/B)
			X (CH_4)** (%)	H_2 Yield (%)	X (CH_4)** (%)	H_2 Yield (%)	
Ex. 4	Ni/Ce-ZrO_2/Θ-Al_2O_3	15	87.1	82.2	87.8	82.2	1.00/1.00
Ex. 5	Ni/La-ZrO_2/Θ-Al_2O_3	12	85.7	81.0	85.5	80.9	1.00/1.00
Ex. 6	Ni-Ca/Ce-ZrO_2/Θ-Al_2O_3	12	83.3	79.9	83.2	79.8	1.00/1.00
Ex. 7	Ni-Mg/La-ZrO_2 /Θ-Al_2O_3	12	80.5	74.2	80.6	74.4	1.00/1.00
Ex. 8	Ni-Ca/Y-ZrO_2/Θ-Al_2O_3	12	81.8	75.8	81.5	76.0	1.00/1.00
Ex. 9	Ni-Ca/Ce-Mg-ZrO_2/Θ-Al_2O_3	12	82.5	78.5	82.3	78.8	1.00/1.00
Ex. 10	Ni-Ca-Cs/La-ZrO_2/Θ-Al_2O_3	12	80.8	76.5	80.7	76.8	1.00/1.00
Com. Ex. 1	Ni/Ce-ZrO_2/Θ-Al_2O_3	2	10.3	10.1	10.5	10.3	1.00/1.00
Com. Ex. 2	Ni/Θ-Al_2O_3	3	75.1	68.0	75.5	68.4	1.01/1.01
Com. Ex. 3	Ni/α-Al_2O_3	15	67.1	54.5	55.1	41.1	0.82/0.75
Com. Ex. 4	Ni/$MgAl_2O_4$	15	81.6	66.8	77.9	72.6	0.95/1.09

*Nickel Content (wt.%): against Θ-Al_2O_3

**X (CH_4): methane conversion

As shown in Table 2, the reforming catalysts according to the present invention showed better activity and stability than those of Comparative Examples. Also, they

have similar trend to that of Table 1.

Ni/Ce-ZrO_2/Θ-Al_2O_3 with 3 wt.% (Example 1) to 15 wt.%(Example 4) of nickel showed initial methane conversion as high as 87-89%. And, the methane conversion was maintained almost after 200min. The initial hydrogen yield was larger than 82%, and was maintained almost after 200min. Also, all of Ni/La-ZrO_2/Θ-Al_2O_3 (Example 5), Ni-Ca/Ce-ZrO_2/Θ-Al_2O_3 (Example 6), Ni-Mg/La-ZrO_2/Θ-Al_2O_3 (Example 7), Ni-Ca/Y-ZrO_2/Θ-Al_2O_3 (Example 8), Ni-Ca/Ce-Mg-ZrO_2/Θ-Al_2O_3 (Example 9) and Ni-Ca-Cs/La-ZrO_2/Θ-Al_2O_3 (Example 10) showed initial methane conversion larger than 80% and initial hydrogen yield larger than 74%. And, they were stable after 200min. Therefore, they have superior property as oxygen reforming catalysts.

On the contrary, Ni/Ce-ZrO_2/Θ-Al_2O_3 (Comparative Example 1) with 2 wt.% of nickel had initial methane conversion and hydrogen yield as low as 10%. They showed significant oxygen reforming activity only when the nickel content was larger than 3 wt.%. Ni/Θ-Al_2O_3 with 3 wt.% of nickel (Comparative Example 2) had 75% of initial methane conversion and 68% of hydrogen yield, which are about 15% lower than those of Example 1 with the same nickel content. Therefore, modified Θ-Al_2O_3 support showed better oxygen reforming activity. Ni/α-Al_2O_3 of Comparative Example 3 and Ni/$MgAl_2O_4$ of Comparative Example 4 showed poor stability with time. In Comparative Example 3, activity after 200min dropped to 82% of the initial activity, and in Comparative Example 4 to 95%. Consequently, the catalyst according to the present invention has superior activity and stability in oxygen reforming, as well as in steam reforming.

Testing Example 3: Determination of reforming activity of nickel catalyst in

steam-oxygen reforming of methane

Steam-oxygen reforming activity of catalysts was determined as follows. The result is summerized in Table 3.

Other conditions were the same as those of Testing Example 1. For the reactant, 2:1:1 mixture of methane:oxgyen:steam was injected into the reactor. The temperature of the reactor was set to 750℃. The space velocity of the gas was controlled to 90,000cc/hr·g-cat with a mass flow controller (MKS Instrument).

Initial activity and activity after catalytic activity 200min were determined at 750℃ and atmospheric pressure by methane conversion and hydrogen yield, as in Testing Example 2. The catalyst activity ratio for methane conversion was determined by Equation 2.

Table 3

Classification	Reforming Catalyst	Nickel Content* (wt.%)	750℃, Initial Activity		750℃, After 200min		Catalyst Activity Ratio (A/B)
			X (CH_4)** (%)	H_2 Yield (%)	X (CH_4)** (%)	H_2 Yield (%)	
Ex. 1	Ni/Ce-ZrO_2/ Θ-Al_2O_3, m	561 3	91.2	102	92.0	102	1.00/1.00
Ex. 2	Ni/Ce-ZrO_2/ Θ-Al_2O_3	6	94.9	101	95.0	103	1.00/1.02
Ex. 3	Ni/Ce-ZrO_2/ Θ-Al_2O_3	12	97.4	104	99.1	107	1.02/1.03
Ex. 4	Ni/Ce-ZrO_2/ Θ-Al_2O_3	15	96.5	102	97.9	104	1.01/1.02

Classification	Reforming Catalyst	Nickel Content* (wt.%)	750℃, Initial Activity		750℃, After 200min		Catalyst Activity Ratio (A/B)
			X (CH_4)** (%)	H_2 Yield (%)	X (CH_4)** (%)	H_2 Yield (%)	
Ex. 5	Ni/La-ZrO_2/ Θ-Al_2O_3	12	89.7	98	90.5	99	1.01/1.01
Ex. 6	Ni-Ca/Ce-Zr O_2/Θ-Al_2O_3	12	92.3	103	92.7	104	1.00/1.01
Ex. 7	Ni-Mg/La-Z rO_2/Θ-Al_2O_3	12	88.5	97	90.0	98	1.02/1.01
Ex. 8	Ni-Ca/Y-Zr O_2/Θ-Al_2O_3	12	89.3	98	89.5	98	1.00/1.00
Ex. 9	Ni-Ca/Ce-M g-ZrO_2/Θ-Al $_2O_3$	12	91.5	102	92.0	103	1.01/1.01
Ex. 10	Ni-Ca-Cs/La -ZrO_2/Θ-Al_2 O_3	12	88.8	97	88.1	97	0.99/1.00
Com. Ex. 1	Ni/Ce-ZrO_2/ Θ-Al_2O_3	2	3.9	4.3	2.2	2.5	0.56/0.58
Com. Ex. 2	Ni/Θ-Al_2O_3	3	3.4	4.8	2.8	4.4	0.82/0.92
Com. Ex. 3	Ni/α-Al_2O_3	15	77.1	81	65.5	68	0.85/0.84
Com. Ex. 4	Ni/$MgAl_2O_4$	15	93.1	97	91.0	95	0.98/0.98

Note:

*Nickel Content (wt.%): against Θ-Al_2O_3

**X (CH_4): methane conversion

As shown in Table 3, the reforming catalysts according to the present invention showed better activity and stability than those of Comparative Examples. Also, they

have similar trend to that of steam reforming and oxygen reforming.

Ni/Ce-ZrO_2/Θ-Al_2O_3 with 3 wt.% (Example 1) to 15 wt.% (Example 4) of nickel showed initial methane conversion larger than 90%. And, the methane conversion was maintained after 200min without deactivation. The initial hydrogen yield larger than 100% was maintained after 200min. The hydrogen yield larger than 100% is due to hydrogen production through water gas shift reaction by carbon monoxide and steam, other than hydrogen production through oxygen reforming. Also, all of Ni/La-ZrO_2/Θ-Al_2O_3 (Example 5), Ni-Ca/Ce-ZrO_2/Θ-Al_2O_3 (Example 6), Ni-Mg/La-ZrO_2/Θ-Al_2O_3 (Example 7), Ni-Ca/Y-ZrO_2/Θ-Al_2O_3 (Example 8), Ni-Ca/Ce-Mg-ZrO_2/Θ-Al_2O_3 (Example 9) and Ni-Ca-Cs/La-ZrO_2/Θ-Al_2O_3 (Example 10) showed initial methane conversion larger than 88% and initial hydrogen yield larger than 97%. And, they were stable after 200min. Therefore, they have superior property as steam-oxygen reforming catalysts.

On the contrary, Ni/Ce-ZrO_2/Θ-Al_2O_3 (Comparative Example 1) with 2 wt.% of nickel had initial methane conversion and hydrogen yield lower than 5%. They showed significant steam-oxygen reforming activity only when the nickel content was larger than 3 wt.%. Ni/Θ-Al_2O_3 with 3 wt.% of nickel (Comparative Example 2) had initial methane conversion and hydrogen yield lower than 5%, which are much lower than those of Example 1 with the same nickel content. Therefore, only modified Θ-Al_2O_3 support shows good steam-oxygen reforming activity. Ni/α-Al_2O_3 of Comparative Example 3 and Ni/$MgAl_2O_4$ of Comparative Example 4 showed poor stability with time. In Comparative Example 3, activity after 200min dropped to 85% of the initial activity, and in Comparative Example 4 to 98%. Consequently, the catalyst according to the present invention has superior activity and stability in steam-oxygen

reforming.

As explained above, modified Θ-Al2O3-supported nickel reforming catalyst according to the present invention is a new-concept nickel reforming catalyst, and if it is used for producing synthesis gas from methane natural gas, methane conversion can be increased in steam reforming, oxygen reforming and steam-oxygen reforming. Also, it has good catalytic stability. And, because inexpensive Θ-Al_2O_3 is used as base support and only small amount of expensive zirconia or other metal components are used, it is very cost-effective.